Aquatic Passive Sampling with Solid-Phase Extraction (In-Situ)
Update – Phase 1 and Phase 2
Central Valley Water Board – United States Geological Survey

With 20 million acres of foothill and forested lands in the Central Valley Region, ensuring protection of our headwater streams represents significant challenges with limited staff resources. Those challenges come in many forms including: the remoteness and difficulty in access; lands that are subject to a multitude of mixed uses with potentially uncooperative landowners; and uncertainties in just what contaminants might be present in surface waters from those varied uses. With such challenges it is easy to see why current grab water sampling methodologies that are dependent upon specific holding times, and lab contracts that require us to know what we are sampling for, might not be the most effective means to allow us to gain a complete understanding of water quality issues in the non-point source (NPS) arena.

Scope of Projects, Including Phase 1

This project is intended specifically to develop a suitable aquatic screening and monitoring tool for NPS discharges, including, but not limited to pesticides used for cannabis production, commercial forestry, and right-of-way (roads and utility corridors). Current technology (grab samples) has relatively high detection limits and is unsuitable for capture of episodic and fluctuating NPS discharge events in remote locations.

Aquatic Passive Sampling using Solid-Phase Extraction (SPE) media is an emerging technology that has been shown to capture NPS discharges – with very low detection limits, and allows sampling for longer duration than that provided by grab samples. In fact, grab sampling has been replaced in many areas of European countries in favor of passive samplers. Passive samplers are durable, require little maintenance, and are easy to pack into remote areas.

The USGS has been using passive samplers in small scale, focused studies to support their Pesticide National Synthesis Project. They have developed a methodology that allows them to configure their chromatography apparatus/equipment to conduct analyte analysis for more than 135 compounds with one sample run. This makes for a powerful screening and monitoring tool.

Currently, the Central Valley Region's Forest Activities Program is working with the USGS to validate SPE sampling methodology on a limited funding basis (Phase 1). The Phase 1 project began with sampling Deer Creek (Tehama County) and Little Cow Creek (Shasta County) in 2017; both creeks provide anadromous salmonid habitat. The USGS recently completed analysis for those deployments with the following results:

Table 1. Phase 1 Results

	Trifluralin	*Dithiopyr*	*Hexazinone*	*Chlorothalonil*
Deer Creek	*3	2	1	2
Little Cow	3		2	2

**Number of sample detections out of four samples deployed at each location.*
Note: results are detections only (mass/disk), not concentrations.
Field blanks used to determine interferences with the samplers or other potential contamination in the field. Lab blanks were used to determine potential lab contamination.

While both creeks provide salmonid habitat, they are dissimilar in many other ways; Deer Creek is a relatively pristine water body with limited commercial timber harvesting activity whereas Little Cow Creek has been heavily affected by agriculture, grazing, rural residential development, roads, etc. Interestingly, as seen in Table 1, three of the four compounds were found in both water bodies. Most notable is the fact there were *no precipitation events or mobilizing flows* for either location prior to or during the sampling events. Samples were collected during summer base-flow conditions in August of 2017. We can postulate that the number of additional detected compounds could likely be higher if sampling were conducted during 'first-flush.'

Compound Information:

- **Trifluralin**: Pre-emergent herbicide that was banned in the European Union since 2008. Has high toxicity to fish and other aquatic organisms.
- **Dithiopyr**: Pre-emergent herbicide.
- **Hexazinone**: Pre-emergent herbicide (heavily used in commercial forestry).
- **Chlorothalonil**: Broad spectrum fungicide, pesticide, acaricide, and used to control mold, mildew, bacteria, and algae. It is highly toxic to fish and aquatic invertebrates. At concentrations of 164 ug/L, it was found to kill a species of frog within a 24-hour exposure. The main breakdown product of chlorothalonil is *4-hydroxy-2,5,6-trichloroisophthalonitrile*, which has been shown to be 30 times more acutely toxic than chlorothalonil and more persistent in the environment.

Phase 2

Additional validation is needed to demonstrate the full capabilities of this technology for distinct applications (e.g., first-flush, storm response sampling, snowmelt, and dry-season sampling). For these reasons, a second phase of the project was developed. After the contract with the USGS is in place, Phase 2 of the project will allow over 90 samples to be analyzed. Based on contract processing and seasonal timing, sampling will likely commence mid-summer 2018. Sampling will focus on sites mainly in the mid-Sierras (Butte County south to Calaveras County) located above the primary watershed reservoir; however additional, specific sampling in other areas will focus on problematic cannabis sites (likely in Region 1).

This second phase of the project will continue to assess the length of time the SPE disks can be held. At this point, we know they can be frozen for months before elution and the eluant can be stored for years before analysis. We will also be testing shipping methods that allow the disks to be sent via postal mail in an inexpensive box with perhaps nothing more than a small cold pack.

It is important to note that this project is specifically working to develop a NPS screening tool, and that this system does not and will not determine concentrations of analytes. This type of screening and monitoring reveals spatial and temporal patterns and detects presence or absence trends over large areas. Positive detections are given as the mass of the analyte accumulated on the SPE media, but cannot tell us when or in what relative quantities the analyte passed through the system. However, relative amounts of analytes captured can show which watersheds have more or less of an analyte than comparison watersheds.

Summary

We recognize that passive samplers have limitations, while they can be left in place for weeks or months and the disks can be frozen making timing of transport to the lab simpler, they do not yet allow for determination of contaminant concentrations. However, given the advancement in the ability to screen for numerous contaminants that passive samplers represent, we expect this technology will substantially increase our

understanding of the state of our surface waters by providing information that can then be used to direct subsequent investigative actions. If, for example, screening conducted where Battle Creek enters the Sacramento River indicates pollutants exist, we could then deploy the samplers upstream to isolate source tributaries for those detected analytes. This would allow us to then direct other, more specific research and sampling methods if numerical concentrations are deemed necessary.